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MODELING OF THE EXTRACTION PROCESS OF TEA SEED OIL WITH SUPERCRITICAL CARBON DIOXIDE

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Abstract - The kinetics of the extraction of tea seed oil with supercritical CO_2 was studied. A kinetic model of the extraction of tea seed oil using supercritical CO_2 was developed on the basis of the differential mass balance to simulate the extraction process. The model could simulate the distribution of the solute concentration in CO_2 inside the extraction bed as a function of extraction time and height of the extraction bed. The model could also simulate of the solute concentration in CO_2 at the outlet of the extractor as a function of time. The effects of the parameters such as pressure and temperature on extraction yield and the process were investigated through the model. This model could simulate satisfactorily the process of extraction with an error between simulation data and experimental data of less than 10%.

Keywords: Supercritical CO_2 extraction; Kinetics; Simulation; Tea seed oil.

INTRODUCTION

Camellia oleifera is the key edible oil tree growing specifically in the south of China. Tea seed oil, a high quality edible oil, is obtained from *Camellia oleifera* seeds. Tea seed oil contains more than 84% unsaturated fatty acids, such as oleic acid, linoleic acid, and linolenic acid, and is characterized by its unique flavor, durable storage, and ease of absorption into the body (Ma *et al*., 2011). It is one of the four edible tree oils (the other three being palm oil, olive oil, coconut oil).

Supercritical CO_2 extraction is a new and green technology for extraction and separation with several virtues such as high efficiency, short extraction time, low operation temperature, less pollution etc.. It has been widely applied in fields such as food, flavor, medicine, etc. Supercritical CO_2 extraction of tea seed oil have been performed by several researchers to study the effects of parameters such as pressure, temperature, extraction time and modifier on the yield and composition of the oil (Rajaei *et al*., 2005; Xu *et al*., 2010; Zhong *et al*., 2001; Zhou *et al*., 2012). Based on our literature survey, no work has been done on the mathematical modeling of the extraction process. Compared with the applied research, the research on the kinetics and mechanisms of dissolution and mass transfer in the extraction of tea seed oil is thus less well developed.

There are three kinds of kinetic models for supercritical CO_2 extraction: empirical kinetic models, kinetic models based on heat transfer and kinetic models based on differential mass balance (Reverchon and Polette, 1996). The simple empirical equation proposed by Naik *et al*. (1989) represents the extraction yield as a function of extraction time in terms of a Langmuir gas adsorption isotherm. Roy and Goto (1996) set up an empirical kinetic model when they extracted oils from ginger root using supercritical fluid. However, in the empirical kinetic

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*To whom correspondence should be addressed model the mechanisms of dissolution and mass transfer are not taken into account (Subra *et al*., 1998; Papamichail *et al*., 2000). Generally the empirical kinetic model is applicable to interpolation not to extrapolation.

In the kinetic model based on heat transfer, the SFE is treated as a heat transfer phenomenon. Each particle of the solute is considered to be a hot sphere cooling in a uniform medium (Li and Qiu, 2007). The model assumes that particles are spherical (Reverchon, *et al*., 1993; Esquivel, *et al*., 1999), which can produce a very big error when the shape of the particles differs greatly from spherical. Secondly, in the models only the effect of diffusion in the particles on mass transfer is taken into account. Thus, the model will not be applicable if substantial mass transfer resistance exists in the fluid phase (Wei *et al*., 2003).

The kinetic model based on differential mass balance centers on mass transfer and can solve the distribution of solute concentration in the fluid phase as a function of height of the extraction bed and extraction time (Reverchon and Marrone, 2001). Therefore, the model fits much research data on the extraction process. Reverchon used the kinetic model based on differential mass balance to model supercritical extraction of clove bud essential oil and sage oil (Reverchon, 1996; Reverchon and Marrone, 1997). However, there are still lots of assumptions in the kinetic models based on the differential mass balance equation, such as particle shape. Some models need to calculate the mass transfer coefficient for comparison with experimental results.

In this paper an improved kinetic model based on the differential mass balance equation is described for the kinetics of extracting tea seed oil with supercritical CO_2, which overcomes the shortcomings listed above. Compared with general models based on differential mass balance, in this model the shape of particles and mass transfer in the solid phase are not taken into account, which facilitates calculation and makes the model more universal. If an artificial neural network were combined with this model, it would predict the extraction yields under other extraction conditions and could play an important role in the scale-up design of extraction process (Fullana *et al*., 1999).

EXPERIMENTAL APPARATUS AND METHODOLOGY

Experimental Apparatus

The experimental apparatus (Huaan Supercritical Fluid Extraction Company, Jiangsu Province, China) has an extractor vessel of 1000 cm^3 and two separators, as shown in Figure 1. Pressure and temperature could be controlled in the extractor and the separators. Operations can be carried out in a closed loop for carbon dioxide, which is recycled as a gas from the last expansion vessel to the pump inlet.

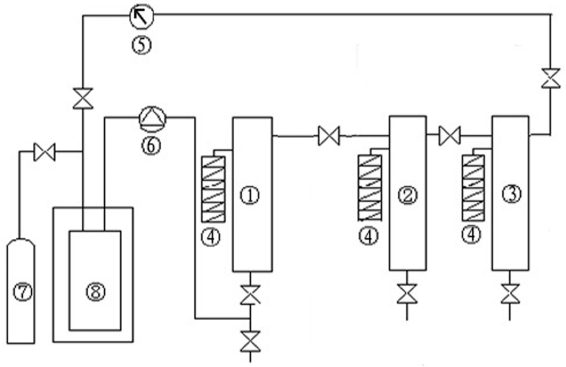


Figure 1: Supercritical CO_2 extraction apparatus: (1) extractor; (2) separator I; (3) separator II; (4) heat exchanger; (5) rotameter; (6) high pressure pump; (7) CO_2 cylinder; (8) CO_2 tank.

Supercritical CO_2 Extraction

The samples were ground and sieved to the same granularity of 20 to 40 meshes. The samples were fed in the extractor and the air in the extractor removed by CO_2. The desired temperatures of extractor, separators, CO_2 tank and heat exchanger were maintained by water baths, respectively. Liquid CO_2 from the CO_2 tank was pumped into the extractor with a high pressure pump. Upon reaching the desired pressure in the extractor and the separators, the extraction started. The extracts were discharged from the separator Ⅰ and the separator Ⅱ every 20 minutes, which were weighed.

MATHEMATICAL MODEL

Many factors affect the extraction process. To simplify the mathematical model, following hypotheses are needed: (a) temperatures and pressures in all parts of the extraction bed are uniform, dissolution and diffusion are carried out in isothermal and isobaric conditions; (b) the velocity and the density of the supercritical CO_2 are constant along the extraction bed; (c) although several components are involved in the extract, their mass transfer behaviors are assumed to be similar, the extract is considered as a single component that is called the “solute” in this paper.

According to the above hypotheses, the differential mass balance of the solute along the extraction bed is given by:

$$\rho\varepsilon\frac{\partial y}{\partial t}+\rho \mathrm{u}\frac{\partial y}{\partial z}-\rho\varepsilon \mathrm{D}_{\mathrm{ax}}\frac{\partial^2 y}{\partial z^2}=J \qquad (1)$$

In Eq. (1), J represents the rate of solute mass transfer from the outer surfaces of seeds to the fluid per unit of bed volume. J will be written in terms of a product of the overall mass transfer coefficient, K, and the specific mass transfer area, A. So, KA will be the mass transfer rate per unit driving force. Since the driving force is y^*-y, J can be written as

$$J=\mathrm{KA}(y^*-y) \qquad (2)$$

The concentration of the oil in the fluid at the entrance of the extractor is zero. It is assumed that y_i is the concentration of the oil at the outlet of the extractor at $t=t_i$. According to the relationship of mass conservation in the extraction bed, the expression for y_i will be written as:

$$y_i=\frac{(dq/dt)_{t_i}}{\mathrm{Q}}\mathrm{q_s} \qquad (3)$$

where (dq/dt) is the rate of oil extraction at time t_i. The value used for KA in the calculations is obtained from the following relationships:

$$y_i\mathrm{Q}=J_i\mathrm{V} \qquad (4)$$

$$(\mathrm{KA})_i=\frac{\mathrm{Q}/\mathrm{V}}{(y^*/y_i-1)} \qquad (5)$$

y^* is the equilibrium concentration of the solute in CO_2 at a certain temperature and pressure. According to Eq. (2), Eq. (3) and Eq. (5) the mass transfer rate, J, can be calculated. Thus, Eq. (1) can be solved using numerical integration with the following initial and boundary conditions.

$$y\Big|_{z,t=0}=0 \qquad (6a)$$

$$\mathrm{u}y\Big|_{z=0,t}-\varepsilon D_{ax}\left(\frac{\partial y}{\partial z}\right)_{z=0,t}=0 \qquad (6b)$$

$$\left(\frac{\partial y}{\partial z}\right)_{z=h,t}=0 \qquad (6c)$$

MODEL PARAMETERS

The average molecular weight of tea seed oil was obtained from Ma *et al*. (2011). The density of supercritical CO_2 fluid was calculated using the Equations of State (EOS) software programmed by David Bush from the Georgia Institute of Technology. The Lucas method was used for viscosity calculation (Poling *et al*., 2001). The axial dispersion coefficient of the solute in supercritical solvent was given by the correlation of Keat *et al.* (Liong *et al*., 1992):

$$D_{ax}=2.42\times10^{-14}M^{-0.48}T/\mu \qquad (7)$$

And y^* was given by the correlation of Valle and Aguilera (1988):

$$y^*=\exp(40.361-18708/T+2186840/T^2)\rho^{10.724} \qquad (8)$$

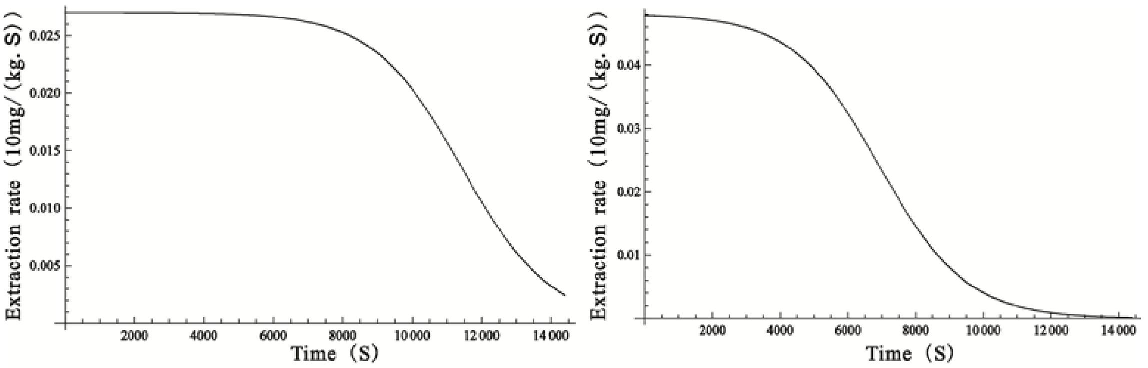
RESULTS AND DISCUSSION

The values of the parameters for the experimental conditions are shown in Table 1 and the calculation and simulation parameters are shown in Figure 2, Figure 3 and Figure 4, at the temperature of 318 K, pressures of 30 MPa and 35 MPa, and a CO_2 flow rate of 20 L/h, using an amount of feed of 200g. Because the pressure and the temperature for extraction of fatty oil are generally from 27 MPa to 35MPa and from 308K to 328K, respectively, we modeled the extraction at a temperature of 318 K and pressures of 30 MPa and 35 MPa. As shown in Figure 2, the extraction rate was maximum at first and, after some time, decreased rather quickly both at 30 MPa and 35 MPa. This is in good agreement with the fact that, in the extraction process, the amounts of the oil extracted were equal in every interval at the beginning and then began to decrease. The extraction process consisted of two extraction regimes, a fast regime and a slow regime, respectively. In the fast regime, the extraction rate was nearly constant. In the slow regime, the extraction rate decreased rapidly. This may be because there was much oil on the surface of particles after grinding and the remaining oil was inside the particles. In the fast regime, the oil on the outside of the particles was easy to extract. The extraction was only affected by the diffusion resistance in the fluid. After the oil on the outside of the particles was extracted completely, it entered into the slow regime, in which the residual oil was inside of the particles. The extraction in the slow regime was affected by the diffusion resistance in the solid particles. Because the CO_2 flow rate of 20 L/h was small, the extraction time approached 4 hours. The extraction rate at 35 MPa and 318 K was greater than that at 30 MPa and 318 K because the solvent power of CO_2 at 35MPa was much greater than that of 30 MPa. As shown in Table 1, at 30 MPa and 35 MPa, the y^* values were 6.89 g/kg and 9.38 g/kg, respectively.

Table 1: Values of the parameters for the experimental conditions.

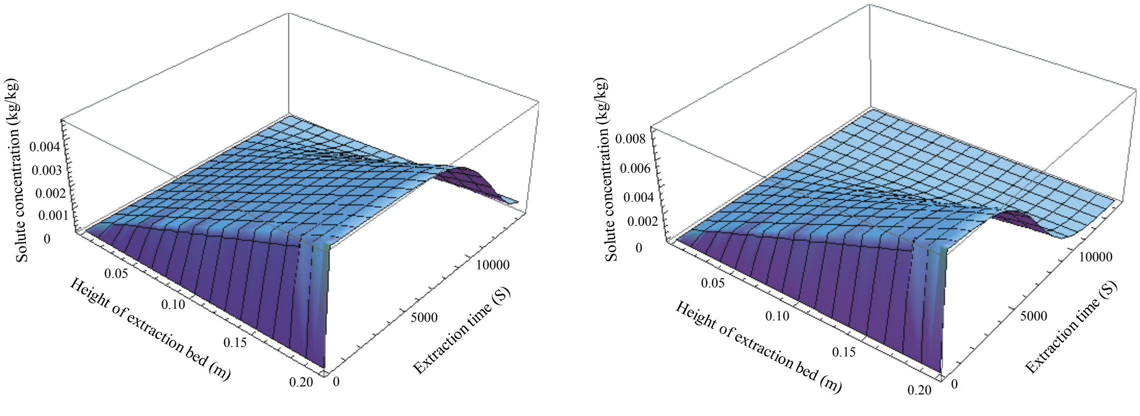
Pressure (MPa)	Temperature (K)	Density of CO_2 (kg/m^3)	Viscosity of CO_2 (10^{-5}Pa/(s))	D_{ax} (10^{-9}m^2/s)	y^* (g/kg)
25	308	903	8.54	5.85	4.85
25	318	858	7.94	6.49	4.54
25	328	812	7.43	7.16	4.13
30	308	930	9.21	5.42	6.65
30	318	892	8.55	6.03	6.89
30	328	851	8.03	6.62	6.83
35	308	954	9.83	5.08	8.74
35	318	918	9.11	5.66	9.38
35	328	882	8.55	6.22	10.02
40	308	973	10.40	4.80	10.80
40	318	941	9.63	5.35	12.23
40	328	908	9.03	5.90	13.68

The distribution of the solute concentration in CO_2 inside the extraction bed as a function of extraction time and height of the extraction bed is shown in Figure 3. The solute concentration gradually increased along the height of the extraction bed. The maximum of the solute concentration was close to the solute concentration in the fluid at saturation, y^*. The solute concentration gradually decreased along the extraction time, the curve being similar to the curve for extraction rate. The distribution of the solute concentration in CO_2 inside the extraction bed as a function of extraction time and height of the extraction bed at 30 MPa and 318 K was only slightly different from that at 35 MPa and 318 K. The extraction at 35 MPa and 318 K had a shorter extraction time and higher solute concentration inside the extraction bed. The solute concentration in the fluid at the outlet of the extractor increased from zero to the maximum in a few minutes, maintained it for a time and then gradually decreased, as shown in Figure 4. The experimental data and values predicted by the model are shown in Figure 5 and Figure 6 at each pressure and temperature, using an amount of feed of 200 g. As shown in Figure 5, at 318 K the extraction yields increased along with the extraction pressure from 25 MPa to 40 MPa, because the solvent power of CO_2 increased along with the extraction pressure. As shown in Figure 6, the effect of temperature on the extraction at 30 MPa was complex. The extraction yield at 318K was higher than that at 308 K or 328 K. On the one hand, as the temperature increases, the density of CO_2 decreases. So the solvent power of CO_2 and the extraction rate decrease. On the other hand, as the temperature increases, the dispersion coefficient increases, which facilitates the extraction. This is in accord with Reverchon and Marron (2001). There was a good agreement between the values predicted by the model and the experimental data, with an error between simulation data and the experimental data of less than 10%. The model reflected well the effects of extraction pressure and extraction temperature on the extraction process and extraction yield.



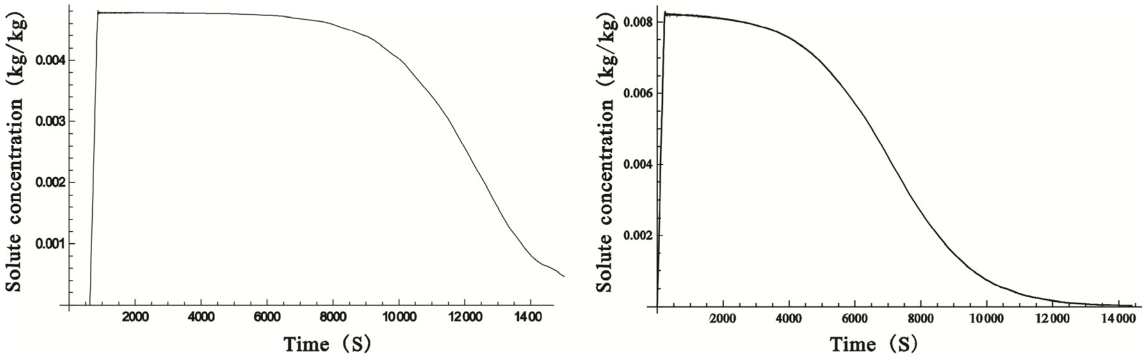
(a) (b)

Figure 2: Curve for the extraction rate at (a) 30 MPa and 318 K and (b) 35 MPa and 318 K.



(a) (b)

Figure 3: Simulation of the distribution of the solute concentration in CO_2 inside the extraction bed as a function of extraction time and height of the extraction bed at (a) 30 MPa and 318 K and (b) 35 MPa and 318 K.



(a) (b)

Figure 4: Simulation of the solute concentration in CO_2 at the outlet of the extractor as a function of time at (a) 30 MPa and 318 K and (b) 35 MPa and 318 K.

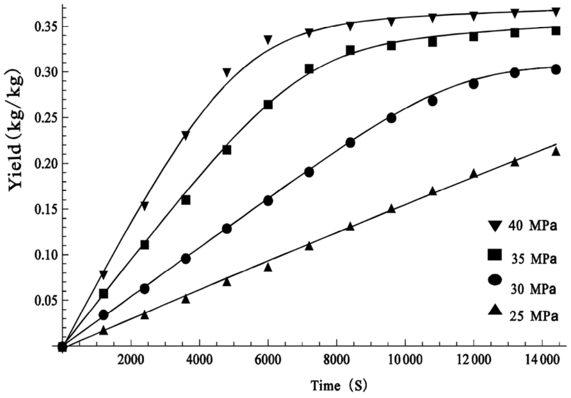


Figure 5: Effect of pressure on extraction at 318 K (Symbols-experimental data; Lines-simulations).

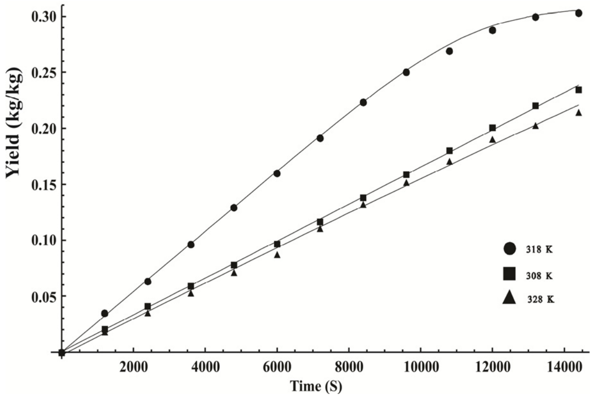


Figure 6: Effect of temperature on extraction at 30 MPa (Symbols-experimental data; Lines-simulations).

CONCLUSION

The model based on differential mass balance adopted in this paper could simulate fairly well the extraction process, in particular the effects of extraction parameters on the extraction process and extraction yield. The model can be applied to simulating the extraction of other vegetable oils. The kinetic simulation of the extraction process can optimize the extraction parameters and aid in industrial scale-up. By inspecting the effects of each operating parameter on the extraction yield and process economy, the parameters can be optimized and, consequently industrial scale-up and optimized operation and control of the production are possible.

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NOMENCLATURE

A	specific mass transfer area (m^{-1})
D_{ax}	axial dispersion coefficient (m^2/s)
h	height of the extraction bed (m)
J	mass transfer rate ($kg/m^3.s$)
K	mass transfer coefficient ($kg/m^2.s$)
Q	CO_2 mass flow rate (kg/s)
q	mass of oil per unit weight of seeds (kg/kg)
q_s	mass of seeds in a differential run (kg)
u	superficial CO_2 velocity (m/s)
V	volume of the extractor (m^3)
y	solute concentration in the fluid phase (kg/kg)
y^*	solute concentration in the fluid at saturation (kg/kg)
z	axial coordinate (m)
ρ	fluid density (kg/m^3)
ε	bed void fraction

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